(12) UK Patent Application (19) GB (11) 2 238 792 (13) A

(43) Date of A publication 12.06.1991

(21) Application No 8920238.6

(22) Date of filing 07.09.1989

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(51) INT CL[5]
C08G 69/42 69/26 69/34, C08L 77/08, C09D 11/10

(52) UK CL (Edition K)
C3R RSM RSX R22D1AX R22D1A2 R22D1BX R22D1B1 R22D1B2 R22D2AX R22D2A1 R22D2A2 R22D2B1 R22D3B R22MX R22M7 R22N1B R22PX
C3V VAE C3W W121 W220 W225 W308 W310
U1S S1390

(56) Documents cited
None

(58) Field of search
UK CL (Edition J) C3R, C3V VACM VACQ VACR VAE
INT CL[4] C08G, C08L, C09D
Online databases: WPI, WPIL

(54) Polyamides

(57) Polyamides are derived from (I) an acid component comprising (a) one or more polymeric fatty acids together with (b) one or more aliphatic monocarboxylic acids; and (II) an amine component comprising one or more polyamines, the aliphatic acid and/or the amine comprising fluorinated compounds. The polyamides are used to produce improved surface properties in coatings derived from printing inks comprising the polyamides as at least a part of their resinous binder constituent, and optionally a colourant.

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POLYAMIDES

This invention is concerned with improvements in and relating to polyamides, to their preparation, and to compositions containing them.

Polyamides derived from, inter alia, polymeric fatty acids (so-called "dimer acids") are widely used as components of printing ink compositions, for example printing inks to be applied by a flexographic process. It is an object of the present invention to provide polyamides of which can impart improved surface properties, e.g. improved resistance to blocking or improved soil resistance, to inks containing them.

Broadly, the present invention provides a polyamide derived from (I) an acid component comprising (a) one or more polymeric fatty acids together with (b) one or more aliphatic monocarboxylic acids; and (II) an amine component comprising one or more polyamines; in which the aliphatic monocarboxylic acids and/or polyamines comprise fluorinated compounds.

The polymeric fatty acid will generally be a polymer, or mixture of polymers, of fatty acids

containing from 8 to 24 carbon atoms. The polymerisation of fatty acids, which may perhaps be better termed as oligomerisation, is a well established process generally leading to mixtures of materials comprising unchanged monomer together with dimer, trimer and higher polymers. A typical polymerisation process involves polymerising ethylenically unsaturated fatty acids, such as oleic or linoleic acids, or mixtures thereof such as tall oil fatty acids, at elevated temperature in the presence of a clay catalyst. Such a polymerisation typically gives a product containing up to 15% by weight of starting monobasic acid (monomer), from 60 to 80% by weight of dibasic acid (dimer), and up to 35% by weight of tribasic and higher acids (trimer and higher oligmers). In view of the relatively high proportion of the dibasic acid or dimer, polymeric fatty acids are generally referred to in the art as "dimer acids" and will, for convenience, be so referred to hereinafter.

The other essential ingredient of the acid component (I) comprises one or more aliphatic monocarboxylic acids. These may, and in accordance with preferred embodiment of the invention do, comprise fluorinated acids. Such acids may be represented by the formula:

$$C_nH_mF_{m'} \quad COOH \qquad (I)$$

(in which n is an integer of from 1 to 24, m is 0 or an integer and m' is an integer and the sum of m and m' is 2n + 1). It is generally preferred that m' be greater than m, that is that the majority of hydrogen atoms in the carboxylic acid have been replaced by fluorine. Typical fluorinated monocarboxylic acids which may be used include $C_8 F_{17} C_2H_4$ COOH and $C_6F_{13}C_{10}H_{20}$ COOH.

The acid component (I) may contain other carboxylic acid species, namely other polybasic and/or monobasic acids. Suitable other such acids include monoaliphatic polybasic acids such as adipic acid and dodecandioic acid; aromatic polybasic acids such as phthalic acid (and its anhydride), trimellitic acid and isophthalic acid; non-fluorinated aliphatic monobasic acids such as acetic, propionic, butyric and isobutyric acids; and aromatic monobasic acids such as benzoic acid and phenylacetic acid.

The dimer acid and aliphatic acids should form a major part of the acid component and, thus, they together suitably form at least 30 %, preferably 60 to 90%, of the acid equivalents in the total acid component.

The amine component (II) comprises one or mor polyamines. The amine component may comprise fluorinated polyamines but, preferably, comprises non-fluorinated compounds. Generally, and preferably, it will comprise a major proportion of diamines, especially aliphatic diamines, for example those of the formula:

$$H_2N.\ C_p\ H_{2p+1}.NH_2 \qquad (II)$$

(in which p is an integer of from 2 to 20). Typical examples of such diprimary diamines include ethylene diamine and hexamethylene diamine. Other diamines which may be used include aromatic diamines such as diaminobenzene The amine component (II) may also comprise other polyamines, e.g. triamines, tetramines, etc. in addition to the preferred diamines. Examples of such other polyamines are aliphatic polyamines of the formula:

$$H_2N(R^1NH)_qH \qquad (III)$$

(n which R' is an ethylene or propylene radical and q is an integer of from 1 to 4). Typical examples of such other polyamines are diethylene triamine and triethylene tetraamine. The amine component may also contain monoamines, for example aliphatic monoamines such as dodecylamine, and aromatic monoamines such as aniline Further, in addition to the acid and amine components discussed above, the polyamide may also be derived from another polyfunctional species, namely an amino acid such as glycine. Generally, however, the use of such amino acids is not preferred and, when used, they suitably form not more than 10%, on an equivalent basis, of the mixture from which the polyamide is prepared.

The relative proportions of the acid and amine components and their individual ingredients, should be such as to give polyamides having the desired molecular weight, acid number, amine number and fluorine content. As is well known, difunctional components (e.g. diacids and diamines) serve to increase the chain length and molecular weight of the polyamide; tri- and higher-functional monomers increase the degree of cross-linking; and monofunctional components, such as monobasic acids and monoamines, serve as chain stoppers to thereby reduce the average molecular weight of the polyamide.

The total f fluorinated components is suitably such that the total fluorine content of the final polyamide is from 1 to 50% by weight, preferably from 4 to 20% by weight.

The relative ratio of total acid groups and total amine groups is conveniently such as to produce a polyamide having an acid value of from 0 to 150 mg KOH/g, and an amine value of from 0 to 150mg KOH/g.

The polyamides of the invention are prepared by reaction of the various acid and amine ingredients discussed above. Typically the reaction is carried out at elevated temperature, e.g. 150 to 250°C, whilst distilling off water produced during the course of the polycondensation reaction. Reaction is suitably effected by bringing the acid component to the desired temperature and then adding the amine component to the heated acid component. If desired, reaction can be carried out in the presence of catalysts such as phosphoric acid and p-toluene-sulphonic acid.

As is conventional with polycondensation reactions, the reaction will be carried out until the final product has the desired acid number and amine number and will gen rally be carried out in the period of from 1 to 8 hours.

As noted above, the polyamides of the invention are particularly useful as ingredients in printing ink compositions. Accordingly a further embodiment of the invention provides a printing ink comprising a resin binder and, optionally, a colourant, in which at least a part of the resin binder comprises a polyamide in accordance with the invention.

The polyamide may form the whole of the resinous binder or may form only a part thereof, in which case it may form a minor part of the resinous binder, e.g. may form as low as 0.1% by weight thereof. A wide variety of other resinous binders may be used in conjunction with polyamide and examples of such include poly(meth)acrylates and copolymers of vinylic monomers; cellulose derivatives such as nitrocellulose and cellulose acetate propionate; polyvinyl butyrate; and non-fluorinated polyamides.

The colourant will generally be a pigment but may also be a dyestuff. In addition to the above ingredients, the ink will also generally contain a solvent or diluent, generally a volatile organic solvent or diluent such as industrial methylated spirits, ethyl acetate, isopropyl alcohol, isopropyl acetate, butyl acetate, toluene, methyl- thyl ketone, _n_-propanol, _n_-propyl acetate and glycol eth rs. The relative

amounts ofthe compounds of the ink should, of course, be such as to give the ink the appropriate rheology characteristics for the desired mode of application of the ink. Thus, a typical ink for application by a flexographic process may comprise from 3 to 60% by weight of resinous binder, from 97 to 40% by weight of solvent and from 0 to 50% by weight of pigment.

When printing inks in accordance with the invention are applied to substrates and dried thereon, the presence of the polyamide of the invention leads to improved surface properties for example as eevidenced by an increased resistance to blocking.

In order that theinvention may be well understood the following example is given by way of illustration only. In the Example all parts are by weight.

Example

A polyamide was prepared from the following ingredients.

Dimer Fatty Acid	99.5 parts
Propionic Acid	9.9 parts
$C_8F_{17}C_2H_4COOH$	10.0 parts
Monomeric Fatty Acid	15.5 parts
Hexamethylene Diamine	15.0 parts
Ethylene diamine	9.5 parts
	159.3 parts

The acids were charged to a reaction vessel fitted with nitrogen sparge and a stirrer. 7.5 of phospheric acid were added as catalyst and silicone antifoam added as required to combat foaming during processing.

The temperature was raised to 60°C and the diamines were added slowly, to prevent excessive exotherm. The temperature was then raised to 130°C and held thereat for 1 hour.

The temperature was then raised to 180-190°C and held until the desired acid and amine value are obtained (Below 6mgKOH/g).

A solution of this polyamide was used to cast a film on a polypropylene substrate and its surface energy compared with a corresponding film prepared from a commercially available conventional polyamide.

Surface energies were measured using Sherman Surface Tension Test Ink pens (Sherman Treaters Ltd, Thame, Oxon OX9 3UW).

Conventional polyamide	36 dynes cm^{-1}
Polyamide of invention	32 " "

CLAIMS:

1. A polyamide derived from (I) an acid component comprising (a) one or more polymeric fatty acids together with (b) one or more aliphatic monocarboxylic acids; and (II) an amine component comprising one or more polyamines; in which the aliphatic monocarboxylic acids and/or polyamines comprise fluorinated cmpounds.

2. A polyamide as claimed in claim 1 in which the fluorinated compound is a fluorinated aliphatic moncarboxylic acid.

3. A polyamide as claimed in claim 1 or claim 2 containing from 1 to 50% by weight of fluorine.

4. A polyamide as claimed in claim 1 substantially as hereinbefore described with reference to the Examples.

5. A printing ink comprising a resin binder and a colourant, in which at least a part of the resin binder comprises a polyamide as claimed in claim 1 or claim 2.

6. A printing ink as claimed in claim 3 substantially as hereinbefore described.

Published 1991 at The Patent Office, State House, 66/71 High Holborn, London WC1R 4TP. Further copies may be obtained from Sales Branch, Unit 6, Nine Mile Point, Cwmfelinfach, Cross Keys, Newport, NP1 7HZ. Printed by Multiplex techniques ltd, St Mary Cray, Kent.